

Research Progress of Preparing Titanium Alloy By Molten Salt Method

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ABSTRACT

Titanium alloy has excellent characteristics that cannot be compared with other metals such as light specific gravity, high specific strength, wide applicable temperature range, corrosion resistance, and hydrogen storage. The traditional titanium alloy smelting process is mainly based on titanium sponge as raw material, which has a long process, high energy consumption, heavy pollution, and other problems, which seriously restricts the sustainable development of titanium alloy in the world. The common methods of preparing titanium alloy are alloy melting, metal thermal reduction, powder metallurgy, and the gradually emerging molten salt electrolysis. Among them, molten salt electrolysis is recognized as the most promising method to replace the traditional titanium alloy production process, and certain achievements have been made in recent years in terms of both process and basic theory research. In this paper, the common processes of titanium alloy preparation by molten salt electrolysis at home and abroad, such as molten salt electrolytic co-deposition method, cathodic alloying method and liquid cathode method, new FFC method, and its derived SOM method, etc., will be summarized systematically, and the future research will be put forward.

KEYWORDS

Titanium alloy; Molten salt electrolysis; FFC; Electro-Co-deposition.

1. INTRODUCTION

The advanced level of titanium industry is an important symbol of a country's comprehensive strength. High-purity titanium has excellent plasticity, sectional shrinkage, machinability and other characteristics, but when it has the presence of impurities become brittle and hard, unsuitable for use as structural materials, so in the machinery manufacturing industry in general use is not pure titanium, but titanium alloys. Titanium alloy integrates the excellent performance of the metal titanium and alloying elements, in the mechanical strength, high temperature strength, corrosion resistance, low temperature performance, etc. are far more than non-alloyed pure titanium materials, and other metal structural materials compared to the density of titanium alloys between aluminium, iron, belonging to the ranks of the light metal materials are known as the "third metal" [1], titanium and titanium alloys in the defence, chemical, metallurgy, biomedical, marine transport, superconducting hydrogen storage and other industries have been widely used and produce good economic benefits. Titanium and titanium alloy in the defence, chemical industry, metallurgy, biomedical, marine transportation, superconductivity hydrogen storage and other industries have been widely used and produced good economic benefits, is a new type of metal resources to promote the development of cutting-edge

technology, with "all-powerful metal" "marine metal" "space metal" It is a new type of metal resource that can promote the development of cutting-edge technology [2], and has the title of "all-purpose metal", "ocean metal" and "space metal" [3]. With the development of science and technology and the improvement of people's living standards, the demand for titanium alloys is growing, titanium alloys have become indispensable materials in various fields, at this stage and even in the future have a broad space for development and application prospects.

At present, titanium sponge, the raw material for the preparation of titanium alloys, is generally produced by the magnesium thermal reduction TiCl_4 process. Metallic titanium powder with titanium sponge as the titanium source, through hydrogenation, atomisation and other powder making methods to produce. Titanium alloy preparation technology is mainly based on the metal titanium powder, the following is a brief introduction to the three traditional methods of preparing titanium alloys: alloy melting method, metal thermal reduction method, powder metallurgy method.

Alloy melting method is to add a variety of metal elements in proportion to the induction furnace, after high-temperature melting to make the corresponding atomic ratio of the alloy, when you can not melt all the raw materials at one time, you need to melt the elements with a high melting point into an alloy, and to get a completely homogeneous alloy needs to be melted several times, resulting in the process flow is long, energy consumption is high and easy to introduce impurities; Metal thermal reduction method uses the metal with greater affinity for oxygen than titanium (generally aluminium metal) as the reductant, rutile or titanium-rich ores such as titanium-iron ore concentrates as raw materials, at atmospheric pressure or vacuum to reduce the metal titanium, titanium and the appropriate amount of molten metal alloying to obtain the corresponding alloy products. This method has a wide source of raw materials, low cost and mature process, but the alloy produced by this method has problems such as low yield of titanium metal, unstable aluminium-silicon content, high consumption of aluminium and excessive oxygen content; Powder metallurgy method is mainly divided into pre-alloying method and mixed element method. Pre-alloying method is to melt titanium sponge and alloying elements at the same time, and prepare pre-alloyed powder by atomisation method and then prepare titanium alloy by isostatic pressure moulding; Mixed element method is the first vacuum dehydrogenation method of titanium powder and alloy powder mixing pressure moulding, and then prepared by vacuum sintering technology. Because it is pressed moulding, so the strength and toughness of the resulting alloy is poor, the alloy volume is small, and the cost of the press mould is high, and it is only suitable for mass production.

The above four methods, such as alloy melting method, metal thermal reduction method, powder metallurgy method, mixed element method, etc. are all based on titanium powder as raw material, and then titanium alloy is prepared by mixing titanium powder with other alloying elements, while titanium powder is processed by titanium sponge and other series of complex processes, the alloy preparation process is cumbersome. Molten salt electrolysis is a more promising method of preparing alloys. The direct preparation of titanium alloys by molten salt electrolysis can eliminate the preparation process of titanium sponge and the process of converting it into titanium powder, and the titanium alloys are directly alloyed in molten salts by co-deposition of titanium ions and alloy ions. Therefore, this paper reviews the commonly used methods for the preparation of titanium alloys by molten salt method, such as molten salt electrolytic co-deposition, cathodic alloying and liquid cathodic methods, the new FFC method and its derivatives SOM method. The preparation of titanium alloys by molten salt electrolysis can simplify the production process of alloys and reduce energy consumption, which is conducive to the further realisation of China's vision of carbon peaking and carbon neutrality.

2. RESEARCH ON THE PROCESS OF PREPARING TITANIUM ALLOY BY MOLTEN SALT ELECTROLYSIS METHOD

The selection of the molten salt electrolyte system has a certain guiding significance for the improvement of product quality and electrolysis process. Various characteristics of the molten salt system are important factors affecting the electrodeposition of molten salt and the selection of a suitable molten salt system. Suitable viscosity of the molten salt facilitates the movement of anions and cations within the electrolyte; The lower the initial crystallisation temperature of the molten salt system (generally the initial crystallisation temperature should be above 50°C), the lower the electrical energy consumption of the electrodeposition system [4]; The higher the conductivity of the molten salt, the higher the current efficiency during electrodeposition. In addition to this, as a basic molten salt electrolyte, it needs to be less corrosive to the electrolyser, non-reactive with anode and cathode products, and easy to prepare at a low cost. The process of preparing titanium and alloys by molten salt electrolysis generally selects halides of alkali and alkaline earth metals as molten salts, with fluorides (e.g., Na₃AlF₆, AlF₃) and chlorides (e.g., NaCl, KCl, CaCl₂) being the most common molten salt systems.

Four methods for the production of alloys by molten salt electrolysis are described below: the molten salt electrolytic co-deposition method, the cathodic alloying method and the liquid cathode method, and the new FFC method and its derivative, the SOM method.

2.1. Molten salt electrolytic co-deposition process

The basic condition to be fulfilled by the electrolytic co-deposition process in the molten salt system is that the deposition potentials of the two metal ions are equal. The principle is the following reaction



The condition $E_{M_1^{n_1^+}/M_1} = E_{M_2^{n_2^+}/M_2}$ must be satisfied. At equilibrium, the deposition potential satisfies the Nernst equation with the following relation:

$$E = E_1^0 + \frac{RT}{nF} \ln \frac{\alpha_{M_1}^{n_1^+}}{\alpha_{M_1}} = E_2^0 + \frac{RT}{nF} \ln \frac{\alpha_{M_2}^{n_2^+}}{\alpha_{M_2}} \quad (3)$$

ever, in the actual electrolysis process, the deposition potentials of the two metals are probably different, so that most alloy electrodeposition is a non-equilibrium process. Considering the role of polarisation and depolarisation, the precipitation potential is equal to the algebraic sum of the equilibrium potential and the polarisation and depolarisation potentials, then the actual co-deposition process should have the following relationship:

$$E = E_1^0 + \frac{RT}{nF} \ln \frac{\alpha_{M_1}^{n_1^+}}{\alpha_{M_1}} + \Delta E_1 = E_2^0 + \frac{RT}{nF} \ln \frac{\alpha_{M_2}^{n_2^+}}{\alpha_{M_2}} + \Delta E_2 \quad (4)$$

This relation shows that the simultaneous discharge of two ions at the cathode involves four aspects: (1) E^0 , the standard precipitation potential of the ions; (2) α , the activity of the ions; (3) the

polarisation potential (overpotential η) on the cathode material during the discharge of the ions; (4) depolarisation (which usually occurs when a solid solution or a compound is formed at the cathode).

In the process of titanium extraction by molten salt electrolysis, an inert electrode (e.g. Mo, W) is used as the cathode, and titanium metal ions and one or more alloying element ions are precipitated together in the form of alloy at the cathode by controlling certain conditions in the electrolysis process. Titanium ions, as the main carriers for electrochemical reactions, are directly involved in the electrochemical reactions in both TiCl_4 and titanate electrolysis, and the deposition behaviour of titanium ions on the cathode directly determines the morphological characteristics of the products.

In addition, by adding active metal chloride (AlCl_3) solid in the molten salt and other ways to use the difference between the electronegativity of different metals and the replacement reaction, the raw material directly in the electrolysis process of chlorination to generate free titanium ions, avoiding the complexity of the preparation process of titanium chloride and is not easy to store and transport the problem.

Beilei Yan [5] prepared TiAl_2 , TiAl_3 alloys by co-deposition of aluminium ions and free trivalent titanium ions during molten salt electrolysis by using AlCl_3 as a source of aluminium ions and chlorinating agent in the NaCl-KCl molten salt system and chlorinating Ti_2O_3 to TiCl_3 by liquid phase reaction; Chenghu Liu [6] carried out co-deposition of zinc-titanium alloys in Urea- ZnCl_2 - TiCl_4 ionic liquid by varying the parameters of substrate, deposition potential, temperature, and concentrations of ZnCl_2 and Ti^{4+} , and obtained uniformly dense zinc-titanium alloys under the condition that the molar fraction of ZnCl_2 was 10%, the temperature was 80°C , and the deposition potential was -1.5 to -2.0V; Polyakova et al [7] prepared Nb-Ti alloys by co-deposition method in $\text{NaCl-KCl-NaF-K}_2\text{NbF}_7\text{-K}_2\text{TiF}_6$ molten salt system and explored the mechanism of electrodeposition; Kun Zhao et al [8] used $\text{KF-KCl-K}_2\text{Ti}_6\text{O}_{13}$ molten salt under Cu electrode at 950°C for electrochemical experiments, Cu-Ti alloys were obtained by constant potential electrolysis of Cu electrodes, and it was noted that Ti^{4+} was reduced to metallic Ti by a two-step mechanism, corresponding to the reduction pathway: $\text{Ti}^{4+} \rightarrow \text{Ti}^{2+} \rightarrow \text{Ti}$. Lijie Qu et al [9] pre-treated titanium substrate at 300V constant voltage and room temperature, on the basis of which calcium phosphate based coatings were prepared on micro-arc oxidised titanium substrate by electrodeposition.

The advantages of the molten salt electrolysis co-deposition method are easy to operate, simple process, can be directly precipitated at the cathode pure metal deposition, and then form alloys and can be observed through the deposition behavior to control the deposition process, to achieve the alloy of the controllable preparation. The disadvantage is that the deposition potentials of the two deposited metals are similar, and during the electrolysis process, the cathode current efficiency is low and the power consumption is large.

2.2. Cathodic alloying and liquid cathode process

Cathodic alloying method adopts one of the components of the alloy as the cathode, other alloy components exist in the molten salt, through electrolysis to make other metal ions diffuse into the cathode to form liquid or solid intermetallic compounds, so as to prepare alloy products with excellent performance. This shows that the cathodic alloying method is divided into "solid cathodic process" and "liquid cathodic process". The "liquid cathode" discharge principle is different from the conventional solid cathode discharge principle, the "electrodeposition process" in the previous section is the titanium ion discharge at the cathode to generate active titanium atoms; The "alloying process" in which active titanium atoms are adsorbed on the surface of a solid cathode and then diffuse into the interior while co-alloying with other alloying atoms. The principle of "liquid cathode" discharge is that titanium ions are discharged on the liquid cathode, and the reduction products diffuse into the liquid alloy while alloying with the cathode alloy element component atoms, i.e. the diffusion process and the alloying process take place at the same time. Due to the difference in the diffusion medium,

the diffusion process in the "liquid cathode" method is very rapid, the alloying process is more rapid and the alloying effect is more uniform.

Liquid cathode method needs to use alloy component elements with low melting point as cathode under high temperature conditions, other components in the molten salt discharge on the surface of the liquid cathode, and the reduction products diffuse to the inside of the liquid alloy, and ultimately form a low-melting-point alloy, so the use of the liquid cathode process for the preparation of alloys is also a method of lowering the melting point of alloys. It's important to note that: (1) The method must be prepared at a temperature higher than the melting point of the cathode material used; (2) In practice, the liquid metal cathode should be placed at the bottom of the crucible, which requires the liquid metal density to be greater than the liquid electrolyte density.

In recent years, the extraction of titanium based on liquid metal cathodes has received much attention. In 2009, Maity et al [10] carried out a study on titanium electrodeposition using a composite of TiO_2 and C as an anode and a liquid Al electrode as a cathode, and the team found that titanium ions can be deposited on liquid aluminium cathodes and produce a titanium-rich phase (i.e., TiAl_2) in the Al electrode. In order to investigate the feasibility of the liquid cathode alloying method for the preparation of titanium aluminium alloys, Beilei Yan put aluminium metal into a small crucible and connected it with a molybdenum wire as a liquid cathode in a molten salt system of NaCl-KCl-TiCl_3 (2 wt.%), and in the experimental process, Ti^{3+} ions were reduced to titanium atoms through two consecutive steps, i.e., $\text{Ti}^{3+} \sim \text{Ti}^{2+} \sim \text{Ti}$, and the titanium alloy started to be formed when the amount of titanium atoms reached. When the amount of titanium atoms reaches enough, titanium-aluminium alloys start to form, and under the stable voltage condition as long as the electrolysis time is long enough, the whole liquid cathode will be alloyed to form titanium-aluminium alloys in the end. Titanium-iron alloys are first-generation hydrogen storage materials, as well as deoxidisers and additives for industrial steelmaking. As one of the most important titanium alloys, conventional titanium-iron alloys are prepared by thermal reduction or mechanical alloying of aluminium, however, the limitations imposed by the price of aluminium and the production of titanium by the Kroll process make the process costly. Based on this background, Jiao Shuqiang's [11] group studied the preparation of titanium-iron alloys by liquid cathode alloying in one-step reduction as an alternative to the conventional process. In this method, iron was selected as the liquid metal cathode and titanium was extracted directly from metal oxides (e.g., ilmenite, rutile, and titanium-bearing metallurgical slag).

Titanium-containing slag ($\text{TiO}_2 > 20\text{wt}\%$) is a valuable secondary resource of titanium. When titanium is extracted by molten salt oxide electrolysis, due to the low theoretical decomposition voltage of titanium, the silicon in the titanium-containing slag will be preferred to titanium to be reduced by electrolysis, which is unfavourable to the extraction of titanium. Pu et al [12] used liquid copper as cathode to extract titanium and synthesise titanium alloys directly from $\text{Al}_2\text{O}_3\text{-MgO-CaO-TiO}_2\text{-SiO}_2$ (decomposition voltages of metal oxides at different temperatures are shown in Figure 1. (a)) electrolyte by molten salt electrolysis, and the experimental setup is shown in Figure 1. (b).

Constant current electrolysis was carried out in $\text{Al}_2\text{O}_3\text{-MgO-CaO-TiO}_2\text{-SiO}_2$ electrolyte with graphite anode and liquid copper cathode. The products after 3 h of electrolysis are shown in Figure 2. (a). The $\text{Al}_2\text{O}_3\text{-MgO-CaO-TiO}_2\text{-SiO}_2$ electrolyte is located at the top of the liquid copper cathode due to the difference in density. The electrolyte is located at the top of the liquid copper cathode. After slicing, the metal-slag in the red area was selected for SEM analysis and a black precipitated phase was present in the copper cathode. As in Figure 2. (a), a line with a length of about $110 \mu\text{m}$ was observed. From the EDS pattern, titanium is mainly present in the precipitated phase. Spot scanning was then carried out to further examine the precipitated phases (points 1 and 3) and the copper matrix (point 2), and it was found that the precipitated phases consisted mainly of copper and titanium, i.e., the formation of a Ti-Cu alloy. The slow diffusion from the interface to the substrate during the electrolysis process results in a significantly larger surface titanium content than the internal titanium content. Titanium is first deposited on the copper surface. Then, during electrolysis, the reduced titanium will diffuse into the bulk of the copper solution to form an alloy, resulting in a Ti-Cu alloy

with a relatively low copper content in the copper matrix. As can be seen from Figure 2. (b), the elements oxygen and carbon are almost absent in the copper cathode and are present only in the slag phase. This indicates that oxygen and carbon are difficult to be introduced into the lumped copper solution. In order to investigate the deposition process of Ti^{4+} in Al_2O_3 - MgO - CaO - TiO_2 - SiO_2 electrolyte, the electrolyte was analysed by XPS. As shown in Figure 2. (c), the valence state of titanium in the electrolyte remains positively tetravalent. The results show that TiO_2 in the electrolyte is directly reduced to zero-valent titanium at the copper liquid cathode. TiO_2 is reduced to titanium metal on a solid electrode by a multi-step reduction process. It is shown that liquid copper cathodes provide better depolarisation than solid electrodes, leading to selective reduction of titanium.

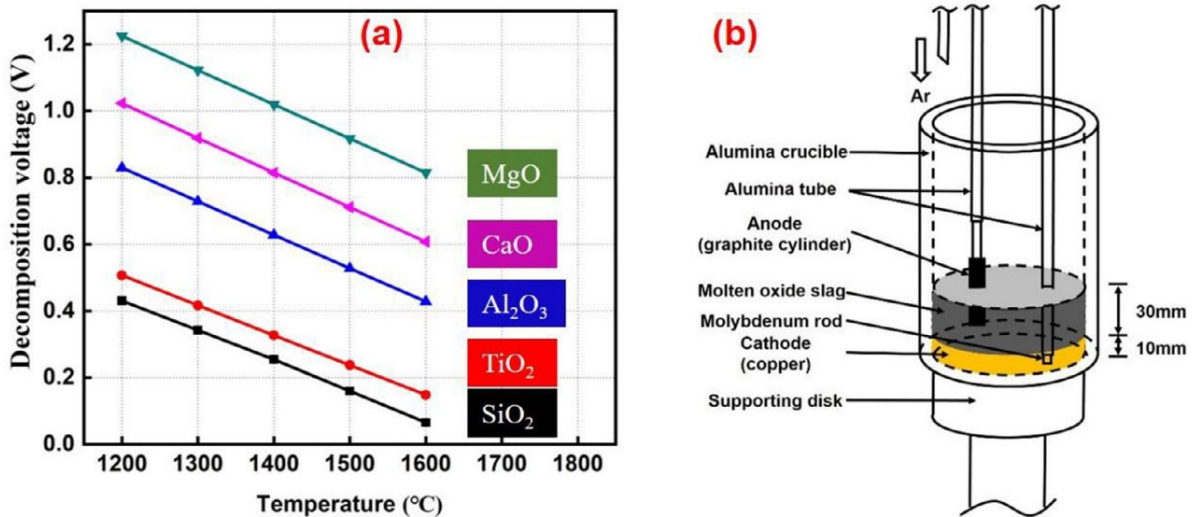


Figure 1. (a) The theoretical decomposition voltages of metal oxides at different temperatures ($MeO+C \rightarrow Me+CO$); (b) Schematic diagram of the experimental device [12]

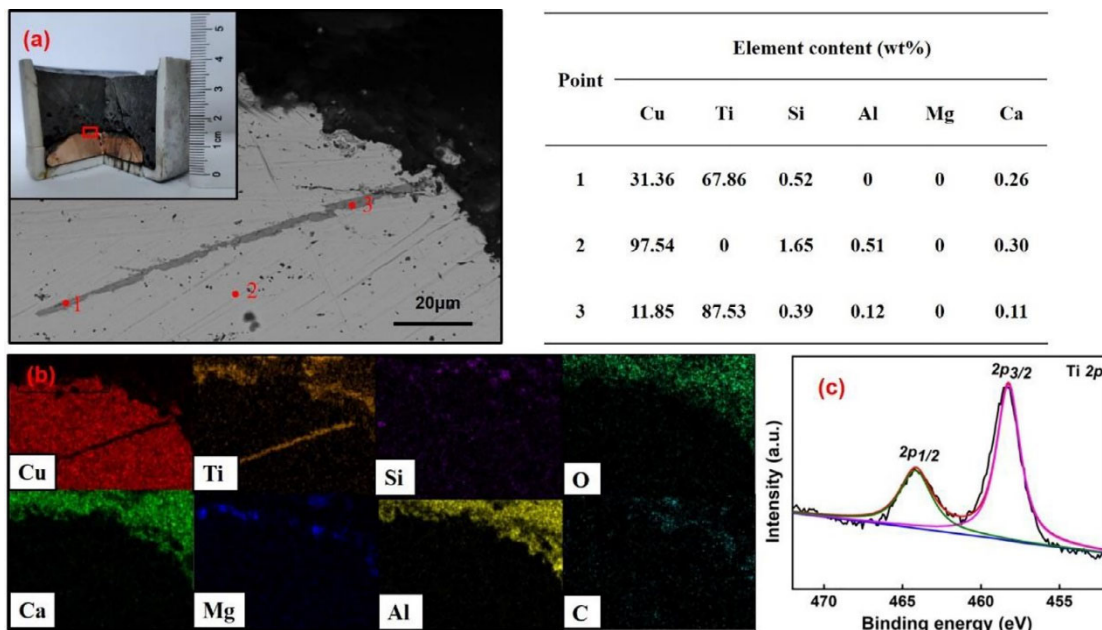


Figure 2. (a) SEM image and (b) EDS images of electrolytic products after galvanostatic electrolysis of 3 h; (c) XPS image of Ti 2p spectrum of the molten Al_2O_3 - MgO - CaO - TiO_2 - SiO_2 electrolyte after electrolysis [12]

Further constant current electrolysis was carried out for 6 h and the electrolysis results were similar to the 3 h electrolysis results. However, Ti-Cu alloys with high titanium content were found on the surface of copper cathodes. Figure 3. (a) shows the SEM image of the copper cathode surface, which shows that a clear metallic phase appears on the copper surface. Copper, titanium and silicon scanned using EDS mapping. Ti-Cu alloys (1, 2) have a high titanium content, however, both the Ti-Cu alloy phase and the copper cathode have a low silicon content. From the XRD spectrum of Figure 3. (b), it can be seen that the diffraction peaks of titanium and copper are obvious, while the diffraction peaks of silicon are very low. The results show that the $\text{Al}_2\text{O}_3\text{-MgO-CaO-TiO}_2\text{-SiO}_2$ electrolyte achieved depolarisation and selective electroreduction of Ti^{4+} on the copper liquid cathode with electrodeposition of titanium predominating. The depolarising effect of copper on TiO_2 is stronger than on SiO_2 . As a result, Ti^{4+} will be preferentially reduced on the cathode copper surface to give Ti-Cu intermetallic compounds directly. However, it can also be noticed from the EDS results that very small amounts of silicon appeared during the long-term electrolysis. The depletion of titanium ions and the decrease in the content of titanium ions in the $\text{Al}_2\text{O}_3\text{-MgO-CaO-TiO}_2\text{-SiO}_2$ electrolyte with the prolongation of the electrolysis time led to the electroreduction of silicon. Experimentally, it is concluded that when liquid copper is used as cathode, the depolarising effect of liquid copper cathode on TiO_2 is greater than that on SiO_2 due to the greater bonding between copper and titanium, the depolarising effect of titanium on liquid copper cathode is enhanced in comparison to that of silicon, and Ti^{4+} can be preferentially reduced, which can be preferentially reduced by one-step electron transfer. In the molten salt electrolysis process, Ti-Cu alloys were firstly prepared from titanium-containing slag, and then Ti-Si alloys were prepared by co-electrodeposition in the oxidised solution with low TiO_2 content. This study provides a specific and effective method for the separation of titanium from titanium-containing slag.

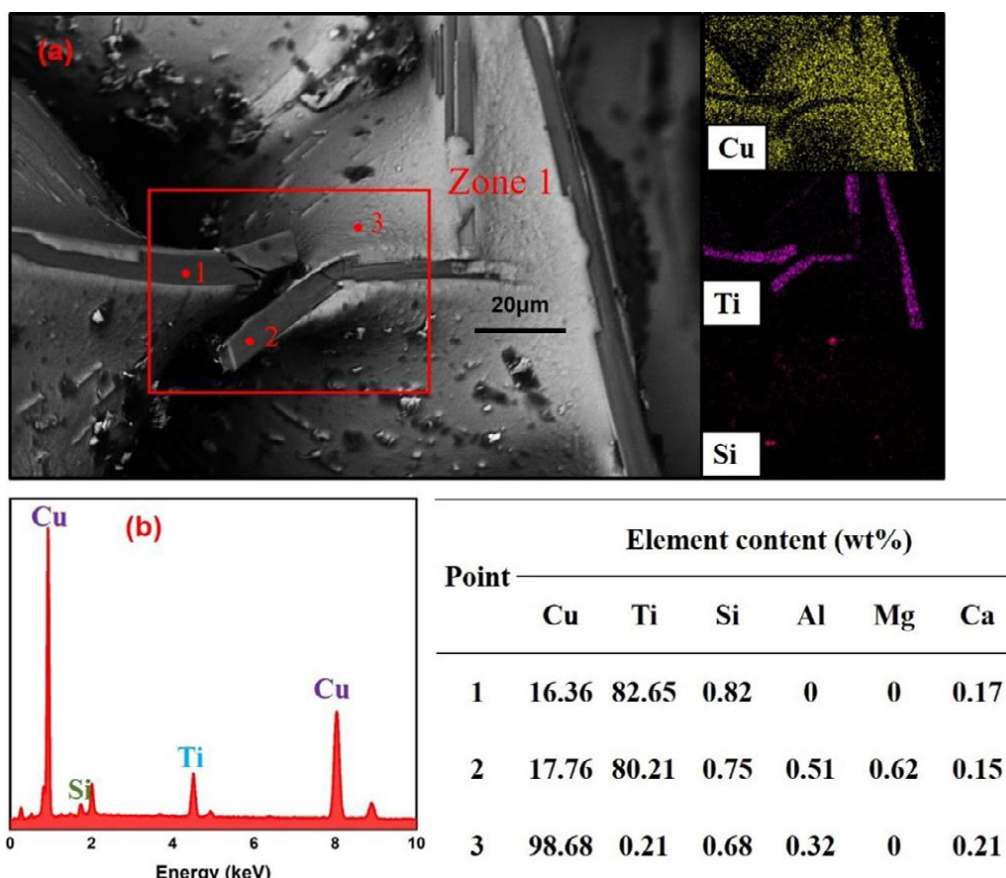


Figure 3. (a) SEM and EDS images of electrolytic products after galvanostatic electrolysis of 6 h; (b) The EDS results of mapping and point scanning of (a) [12]

The advantage of the liquid cathode alloying method is that it is commonly used to prepare binary and polymer alloys, so that the resulting alloys are homogeneous in composition, free of segregation, and can be used as a feedstock for other applied alloys. The disadvantage is that when constant current electrolysis is carried out at the liquid cathode, the density of the current affects the composition of the alloy.

2.3. New Molten Salt Electrolysis FFC Process

In 2000, three scholars, Fray, Farthing and Chen from the University of Cambridge [13] firstly proposed the Cambridge method of direct electrolytic preparation of titanium metal using solid titanium dioxide as the cathode (FFC method), and the FFC Cambridge method uses direct reduction of TiO_2 to make the separation of oxygen and titanium to prepare titanium metal or titanium alloy. Compared with the traditional molten salt electrolysis method, the use of more common and cheaper titanium dioxide as raw material reduces the production cost and avoids the strong corrosiveness brought by the use of TiCl_4 material; the solid oxide one-step deoxidation to extract titanium reduces the reaction temperature, shortens the process and improves the production efficiency; and the process no longer produces hazardous chlorine gas, which is More environmentally friendly. It is an epoch-making green production method of titanium and titanium alloy. The FFC method electrolytic cell setup is shown in Figure 4.

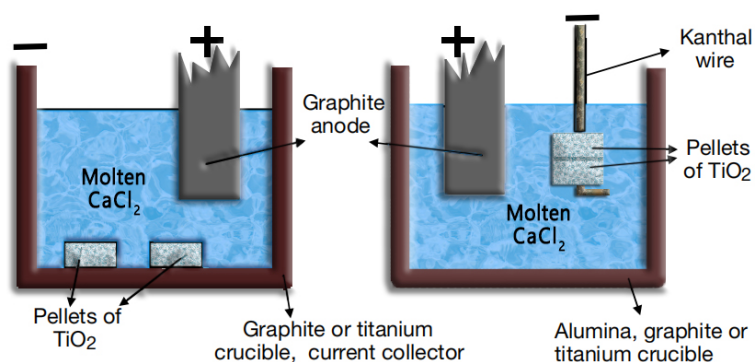
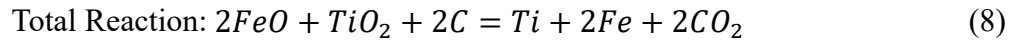
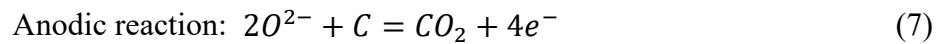
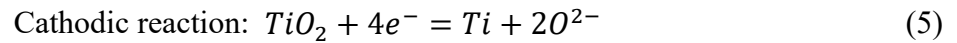


Figure 4. Schematic diagram of FFC method electrolytic cell [14]

For the preparation of titanium alloys by the FFC method, Chen Zhiyuan et al [15] showed that the KCl-NaCl-CaCl_2 ternary system can be used as the basic ternary system for the production of titanium metal or titanium alloys by electrodeoxygenation, and the raw materials enriched with titanium elements are generally pressed into the cathode sheet, with the carbon rods as the consumable anodes, and CaCl_2 , which is of high oxygen solubility, is selected as the molten salt system. It should be noted that: in the process of electrodeoxygenation, the electrolysis temperature must be higher than the melting point of the molten salt, the electrolysis voltage must be higher than the decomposition voltage of titanium oxide and lower than the decomposition voltage of the molten salt; the preparation of cathode is the key to the success of electrodeoxygenation, and the differences in the ball milling, pressing, and sintering processes affect the particle size composition of the cathode material, the porosity, and the electrical conductivity, in order to safeguard the porosity and mechanical strength of cathode, the general control of the particle size is at the micrometer level, and the pressure of the press is controlled at the range of 10 to 15 MPa [16]. The appropriate sintering temperature is conducive to increasing the porosity and effective reaction area of the samples, and the mechanical properties of the pressed tablets were improved after sintering, with a more homogeneous composition, which helps to improve the electrolysis efficiency. Titanium-containing blast furnace slag is the main solid waste from blast furnace ironmaking, and is a by-product of ironmaking from

vanadium-titanium magnetite. Which contains a large amount of titanium dioxide, but due to the lack of effective treatment methods, resulting in a large number of titanium resources can not be effectively utilised can only be discarded and stockpiled, resulting in a waste of titanium resources at the same time to the environment has brought great pressure [17]. Dai Wei et al [18] used high titanium slag as raw material to prepare titanium alloy by FFC molten salt electrodeoxygenation method, by studying the reaction course of electrolysis in CaCl_2 molten salt to prepare titanium-iron alloys, the optimum reaction conditions were determined to be the electrolysis temperature of 850°C , the tank voltage of 2.8 V, and the electrolysis time of 8h, and Ti-Fe alloys were successfully prepared under these conditions. High titanium iron refers to titanium-iron alloys containing about 70% titanium, which are indispensable quality-oriented alloys for smelting high-quality steel grades. Li Qingyu et al [19] used a mixture of titanium concentrate and titanium dioxide (Ti: Fe=3:1) as raw material to produce a high titanium-iron alloy in one step by electrochemical reduction, and the alloying process is as follows: TiO_2 is firstly reduced to CaTiO_3 , and then continues to be deoxidised and reduced to titanium metal; ilmenite is preferentially reduced out of the metal iron and the resulting titanium metal to produce titanium-iron alloy by alloying reaction. Yang Xu Liu [20] conducted an experimental study on the formation mechanism of CaTiO_3 and obtained that CaTiO_3 is formed by two pathways: (1) the molten salt is involved in the reaction and is the main cause of the reaction, and (2) the hydrolysis of the molten salt CaCl_2 yields CaTiO_3 . The principle of preparing titanium-iron alloy by molten salt electrolysis is as follows:



Ruimeng Shi et al [21] tried to use oxide ore as raw material for molten salt electrolysis experiments, and directly used Panzhihua titanium concentrate for molten salt electrolysis to prepare titanium-iron alloys, in order to achieve the purpose of saving cost and reducing environmental pollution. The experiments used molten and then re-solidified titanium concentrate as the cathode to investigate the formation mechanism of Ti-Fe alloys during electrolysis and the influencing factors of the formation rate. The rate of Ti-Fe alloy preparation by electrolysis of titanium concentrate is determined by four aspects: (1) the rate of oxygen migration to the cathode surface through the reduction layer; (2) the rate of oxygen ion migration to the anode through the electrolyte; (3) the rate of cathodic electrolytic reduction; and (4) the rate of titanium and iron alloy formation. The rate of electrodeoxygenation can be improved by modifying the cathode. Wang Bo et al [22] used the FFC method of electrolysis of titanium-containing slag to investigate the effect of cathode doping with different carbon content on the rate of electrodeoxygenation as. It was found that cathode doping with carbon powder is beneficial to improve its electrochemical activity, and when the doping amount of carbon powder is 5%, the electrolysis product has the most uniform particle size, higher Ti content, and better deoxygenation effect.

Compared with titanium-iron alloys, titanium-silicon alloys have the excellent properties of high melting point and the ability to maintain stable strength for a long period of time at high temperatures, making them a good high-temperature resistant structural material. Bing Zhang [23] of Northeastern University prepared titanium-silicon alloys by the FFC method and found that the alloying reaction of titanium-silicon went through four stages successively, $\text{Ti}_5\text{Si}_3 \rightarrow \text{Ti}_5\text{Si}_3 + \text{TiSi} \rightarrow \text{TiSi}_2 \rightarrow \text{TiSi} + \text{Si}$.

Zhongren Zhou [24] prepared silicon and titanium alloys by molten salt electrolysis using a pre-sintered $\text{SiO}_2/\text{TiO}_2$ mixture as the cathode and thermodynamic calculations showed that the monomorphous silicon and monomorphous titanium generated at 700°C can spontaneously undergo alloying reactions to produce silicon and titanium series alloys, and tend to produce TiSi_2 alloys. Electrolytic reduction of TiO_2 on the basis of monomeric Si yields TiSi_2 , while SiO_2 on the basis of monomeric Ti yields Ti_5Si_3 alloy [25]. Qiang Ma of Chongqing University [26] used the FFC method to prepare Ti_5Si_3 and investigated the electrolysis process of the prepared cathode sheets under different conditions, the results show that the higher the sintering temperature of the cathode sheet the faster the electrolysis rate; When the thickness of the cathode sheet used is increased, the composition of the physical phases of the inner and outer layers does not coincide, and the analysis shows that the reaction proceeds from the outside to the inside; the longer the electrolysis time, the more Ti_5Si_3 is present in the product, controlling the other variables constant.

To address the question of whether the alloy composition in the alloying product is controllable, Meifeng Liu et al [27] chose a mixture of TiO_2 and Cr_2O_3 with a molar ratio of 1:1 as the cathode, and electrolysed it for 6 h at a tank voltage of 2.8 V to obtain a Ti-Cr alloy with an oxygen content of 0.20%, and the mixture of titanium dioxide and chromium oxide was reduced to an alloy with a molar ratio of Cr to Ti that was close to the raw material's molar ratio, which indicated that the molten salt electrolysis of titanium-chromium mixed oxides can directly prepare titanium-chromium alloys with controlled composition. Jihong Du et al [28] investigated the preparation process and mechanism of Ti-V alloys prepared by molten salt electrodeoxygenation, and the experimental results showed that the reaction process is an alloying process from preferential generation of titanium from mixed oxides to gradual reduction into Ti-V alloys with controllable components.

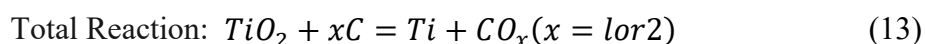
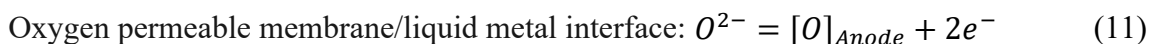
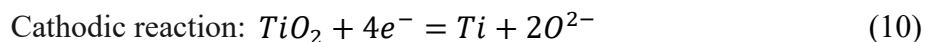
FFC process advantages: (1) The FFC method shows a new extraction concept and a good development prospect; (2) the process is simple; (3) the reaction temperature is low, generally in the range of $800\sim 1000^\circ\text{C}$; (4) the production cost is low, the raw material is easy to obtain, and the electrolyte is cheap; (5) it is green and environmentally friendly, and can be realised as a continuous production; and (6) it can be used to prepare difficult-to-produce metals or alloys. Such as Ti-Ni memory shape alloy. The production of such alloys is not easy due to the difficulty in controlling the ratio of raw material components and alloy density. If the FFC method is used, as long as the amount of TiO_2 and NiO_2 in the raw material is proportioned according to the required alloy composition when making the cathode sheet, the alloy with the required composition can be obtained through electrolysis.

Of course, the FFC process has some drawbacks, as follows: (1) The mechanism of electrolytic deoxygenation by the FFC method has not been clarified, and the electrolysis process conditions affecting the electrolysis process need to be explored using the knowledge of thermodynamics and kinetics. (2) The efficiency of electrodeoxygenation by the FFC method is very low, and since graphite is used as the anode in this method, the ablation of graphite aggravates the side effects of the electrolysis process, and even leads to short-circuiting of the current [29]. (3) The potential is not easy to control, TiO_2 itself is not conductive, only at the beginning of the electrolysis to apply a large voltage, so that some of the oxygen atoms dissociated to conduct electricity, and to control the potential to ensure that titanium metal precipitation of the molten salt is not electrolysed is still a difficult point. (4) The deoxidation of different metals in the alloy, metal alloying, and the homogenisation of the alloy composition in the preparation of alloys by the FFC method need further study.

2.4. Improved FFC process SOM process

The SOM method proposed by Professor U.B Pal [30] of Boston University in 2001 is a green, energy efficient extraction metallurgy technology, the main difference between this method and the FFC Cambridge method is that the anode of the SOM method uses a solid oxygen permeable membrane

with good high temperature and corrosion resistance to separate the anode material from the electrolyte. The solid oxygen permeable membrane is selective to anions, only oxygen ions can migrate to the anode to participate in the electrode reaction under the action of electric field, so we don't have to worry about the discharge of other anions to produce harmful gases. Molten salt electrolysis TiO_2 electrolysis schematic diagram and electrolysis principle is shown below:



SOM method is essentially a new metallurgical process with short flow, high efficiency, energy saving and environmental protection, which is formed after improvement on the basis of FFC method. SOM method can prepare metals, alloys and metal carbides from metal oxides or composite ores by direct electrolytic deoxidation; it does not consume anode and can effectively avoid anode side reaction and anode products; the presence of oxygen permeable film can avoid molten salt decomposition, so it can be operated under the applied voltage which is higher than the decomposition voltage of the molten salt electrolyte, which improves the efficiency of the reaction; isolation of other ions as well as molten salts effectively avoids the problem of cathodic products being contaminated, and improves the purity of the products. Yuanyuan Shen et al [31] applied the SOM method to the recycling of superfine titanium slag. The experiments were carried out using the round flake solid of superfine high titanium slag after moulding and sintering as the cathode and the solid oxygen permeable membrane tube containing carbon saturated copper liquid 8Y-ZrO₂ as the anode, and electrolysis was carried out at 1100°C and 3.5 V tank voltage to finally obtain titanium metal.

The SOM method can be applied not only to the preparation of titanium metal but also to the preparation of the corresponding titanium alloys by direct electrolysis of oxide complex ores. In recent years, good progress has been made in the study of metal and alloy preparation from molten salt electrolysis of metal oxides, which provides a new idea for the direct extraction of metals and alloys from oxide composite ores in a short process. At present, the group of Xionggang Lu [14] has successfully prepared titanium metal, titanium-silicon alloys, titanium-iron alloys [32], etc., based on the SOM method a, using the structure of the experimental device b as shown in Figure 5. Xionggang Lu [33] group by using the SOM method of direct electrolysis of titanium-containing composite ore to prepare Ti₅Si₃ alloy, the surprise discovery of the electrolysis process of the impurity metal elements Ca, Mg, Al, etc. have been effectively removed, to solve the titanium-containing blast furnace slag in the separation and removal of impurity metal ions in the difficult problem. In 2010, they applied the SOM method to the electrolytic treatment of Panzhihua titanium-containing blast furnace slag in high-temperature molten salt and obtained a relatively pure titanium-silicon series of alloy products, which provides a more efficient and environmentally friendly way for the development of a large number of low-grade deposits of high-value-added metals in the Panzhihua area [34].

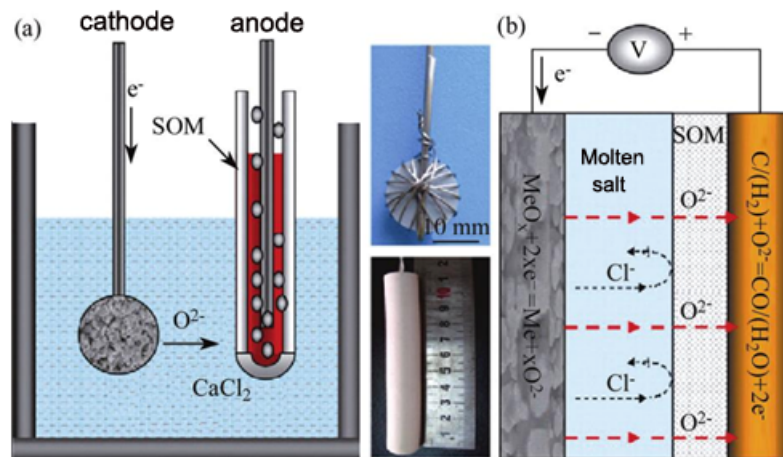


Figure 5. (a) Schematic diagram of SOM method electrolytic cell and (b) Schematic diagram of the principle of SOM method [14]

In order to explore the relationship between the product composition's and the raw materials, and then achieve the controllability of the product alloy composition. Xionggang Lu et al [35] used the SOM method to prepare titanium silicide intermetallic compounds by direct electrolysis of TiO_2 and SiO_2 mixed powder as raw materials. And concluded that the molar ratio of raw materials plays a dominant role in the composition of the final product. The group also used the SOM method for the synthesis of $\text{Ti}_5\text{Si}_3/\text{TiC}$ composites by direct molten salt electrolysis [36]. The experiments were carried out using a mixture of TiO_2 , SiO_2 and C powders pressed into a solid as a cathode. The results show that (1) the membrane-based anode electrolysis system has higher current efficiency and reduction rate compared to the common graphite anode electrolysis system, and (2) the SOM method is demonstrated to be a promising low-energy-cost and environmentally friendly electrochemical method for the production of carbide alloys, such as $\text{Ti}_5\text{Si}_3/\text{TiC}$ composites.

The advantage of the SOM method over the FFC method is that the SOM method breaks the condition that the solvent is not allowed to contain metal ions with a higher precipitation potential than the metal to be obtained. This method, due to the presence of a solid oxygen permeable membrane, allows only oxygen ions to be precipitated on the anode during the entire electrolysis process, so the substances involved in the electrolysis reaction are oxides. Under the condition that the solvent is non-oxide, the solvent will not be electrolysed even if the electrolysis voltage is increased. The disadvantage is the high temperature requirement, which needs to satisfy the melting point of the molten salt system as well as the oxygen permeability of the solid oxygen permeable membrane, and the experiments are best performed at 1100°C to 1300°C [14, 29].

3. CONCLUSIONS AND OUTLOOK

Since the traditional titanium alloy production process has problems such as long process, complicated process and low utilisation of raw materials, which causes serious waste of titanium resources and high price of raw materials, it is of great significance to study the preparation process of new titanium alloys. The preparation of titanium alloy by molten salt electrolysis is the most likely method to replace the traditional titanium alloy production process, and the preparation of titanium alloy by molten salt electrolysis can significantly shorten the process flow and improve the utilisation rate of titanium resources. At present, there are still many problems in the research of liquid cathode alloying and electrolytic co-deposition process, such as the specific diffusion kinetic process of titanium in liquid metal, whether the liquid metal cathode can maintain the liquid activity during a long period of electrolysis, and the optimisation of the alloying process, etc. By improving and optimising these problems, it will be possible to realise the industrial production of titanium alloys

prepared by molten-salt electrolysis in a matter of days. Both FFC and SOM methods use solid titanium oxide or titanium-containing minerals as raw materials for one-step electrolytic preparation of titanium alloys, which greatly shortens the preparation process, reduces the content of impurities, and meets the strategy of green sustainable development compared with the traditional electrolytic process. However, most of the current studies on the preparation of titanium and titanium alloys by electrolysis remain at the laboratory stage, and the application of industrial production is immature, therefore, to realise the goal of the industrial production of titanium alloys by molten salt electrolysis method, further studies are still needed.

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